CHM 305 Problem Set 4

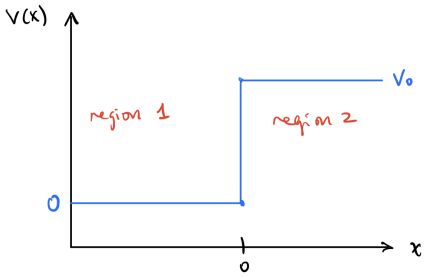
Distributed: Tuesday, October 6, 2026
Due: Monday, October 12, 2026 @ 11:59 PM ET

Problem Set Submission: Please submit assignment by uploading your files to Canvas. You may upload scanned handwritten work or digital documents as .pdf files.

Collaboration & AI Policy: Collaboration with classmates is encouraged to aid in learning and understanding the course material and homework problems, but your written solutions must be produced independently and reflect your own, independent understanding. Consulting general textbook and online references is fine while working through problem sets, but seeking out explicit solutions to any problems (by consulting, e.g., textbook solutions, discussion forums, online platforms like Chegg, generative AI, or agentic AI) is strictly prohibited.

1 The Finite Step Potential

In this problem, we will consider what happens when a quantum particle hits a finite potential barrier. We will determine the probabilities that the particle is reflected versus transmitted. Consider a particle moving towards a finite step in the potential, as we discussed in class in Lecture 7:



$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x \geq 0 \end{cases}$$

where V_0 is a constant. As we discussed in class, if we have a particle approaching the step from the left with energy $E > V_0$, then the solutions to the Schrödinger equation in the two regions are:

$$\psi_1(x) = Ae^{ik_1 x} + Be^{-ik_1 x} \qquad \text{for } x < 0$$

$$\psi_2(x) = Ce^{ik_2 x} \qquad \text{for } x > 0$$

where

$$k_1 = \left[\frac{2mE}{\hbar^2}\right]^{1/2} \quad \text{and} \quad k_2 = \left[\frac{2m(E - V_0)}{\hbar^2}\right]^{1/2}$$

Here e^{ikx} terms represent a particle traveling to the right and e^{-ikx} terms represent a particle traveling to the left. The coefficients A, B, and C encode the probabilities that a particle is traveling in a certain direction in a given region. For example, $|A|^2$ represents the probability that the particle is in Region 1, traveling towards the right with momentum $+\hbar k_1$.

If we consider N particles exploring this landscape, then we can interpret the quantity $|A|^2 N$ to be the number of particles with momentum $\hbar k_1$ in Region 1. The number of these particles that pass a given point per unit time is given by $v|A|^2 N$, where the velocity v is given by $\hbar k_1/m$ in Region 1 and $\hbar k_2/m$ in Region 1.

(a) $\psi(x)$ and $\frac{d\psi}{dx}$ must be continuous at $x = 0$. In other words,

$$\psi_1(0) = \psi_2(0)$$

$$\left.\frac{d\psi_1}{dx}\right|_{x=0} = \left.\frac{d\psi_2}{dx}\right|_{x=0}$$

Use these boundary conditions to derive the following system of equations:

$$A + B = C$$

$$k_1(A - B) = k_2 C$$

(b) Now, let's define the reflection coefficient r

$$r \equiv \frac{\hbar k_1 |B|^2 N/m}{\hbar k_1 |A|^2 N/m} = \frac{|B|^2}{|A|^2}$$

which represents the probability that a particle striking the step from the left will be reflected back into Region 1. Use the system of equations from part (a) to show that:

$$r = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2$$

(c) Similarly, let's define the transmission coefficient t

$$t \equiv \frac{\hbar k_2 |C|^2 N/m}{\hbar k_1 |A|^2 N/m} = \frac{k_2 |C|^2}{k_1 |A|^2}$$

which represents the probability that a particle striking the step from the left will be transmitted into Region 2. Use the system of equations from part (a) to show that:

$$t = \frac{4k_1 k_2}{(k_1 + k_2)^2}$$

(d) Use the expressions from parts (b) and (c) to show that $r + t = 1$. Why should we expect this to be the case?

(e) Show that $r \to 0$ and $t \to 1$ as $V_0 \to 0$. Why should we expect this to be the case?

2 Quantum Harmonic Oscillator Wavefunctions

The first few eigenfunctions of the quantum harmonic oscillator are

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x\, e^{-\alpha x^2/2}$$

$$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1)\, e^{-\alpha x^2/2}$$

recalling that we defined $\alpha \equiv \left(\frac{k\mu}{\hbar^2}\right)^{1/2}$ for compactness.

(a) Sketch $\psi_0(x)$, $\psi_1(x)$, and $\psi_2(x)$.

(b) In class, we verified that the ground state wavefunction $\psi_0(x)$ satisfied the time-independent Schrödinger equation. Verify that $\psi_1(x)$ satisfies the Schrödinger equation as well.

(c) Recall that eigenfunctions of the same Hamiltonian should be mutually orthogonal. Show that $\psi_0(x)$ is orthogonal to both $\psi_1(x)$ and $\psi_2(x)$ by explicit integration. *Hint:* Consider the useful properties of even and odd integrands:

$$\int_{-\infty}^{\infty} f(x)dx = 0 \qquad \text{for } f(x) \text{ odd}$$

$$\int_{-\infty}^{\infty} f(x)dx = 2\int_{0}^{\infty} f(x)dx \qquad \text{for } f(x) \text{ even}$$

The following Gaussian integrals may also come in handy, where n represents a positive integer:

$$\int_0^\infty e^{-\alpha x^2} dx = \left(\frac{\pi}{4\alpha}\right)^{1/2} \tag{1}$$

$$\int_0^\infty x^{2n} e^{-\alpha x^2} dx = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}\alpha^n}\left(\frac{\pi}{\alpha}\right)^{1/2} \tag{2}$$

$$\int_0^\infty x^{2n+1} e^{-\alpha x^2} dx = \frac{n!}{2\alpha^{n+1}} \tag{3}$$

Note: Use Eqn. (2) for even powers of x, and Eqn. (3) for odd powers of x.

3 Expectation Values and Uncertainties for the Quantum Harmonic Oscillator

(a) Compute $\langle x \rangle$, $\langle p \rangle$, $\langle x^2 \rangle$, and $\langle p^2 \rangle$ for the $\psi_0(x)$ ground state of the quantum harmonic oscillator given in the previous problem. Use symmetry when you can, but carry out explicit integration where needed. You may want to make use of the Gaussian integrals given in the previous problem.

(b) Check the uncertainty principle for the $\psi_0(x)$ HO state by examining $\sigma_x \sigma_p$. Where does this quantity fall compared to the position-momentum uncertainty limit of $\hbar/2$ that we derived in class?

(c) Compute the expectation values of the kinetic energy and potential energy for the $\psi_0(x)$ HO state, by evaluating:

$$\langle KE \rangle = \left\langle \frac{p^2}{2\mu} \right\rangle$$

$$\langle V \rangle = \left\langle \frac{1}{2} k x^2 \right\rangle$$

(d) Is the sum of $\langle KE \rangle$ and $\langle V \rangle$ what you would expect?

4 The Time-Dependent Harmonic Oscillator

A particle in a harmonic oscillator potential starts out in the initial superposition state

$$\Psi(x, 0) = A \left[3\psi_0(x) + 4\psi_1(x) \right]$$

(a) Find A to normalize the wavefunction.

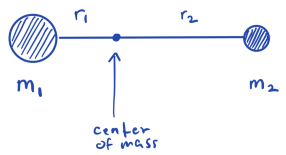
(b) Write down expressions for $\Psi(x, t)$ and $|\Psi(x, t)|^2$.

You will find that $|\Psi(x, t)|^2$ oscillates at exactly the classical harmonic oscillator frequency! That's interesting, but consider: what frequency would the system have oscillated at had we specified $\psi_2(x)$ in the initial superposition state instead of $\psi_1(x)$?

(c) If you measured the energy of this particle, what values might you measure, and with what probabilities?

5 The Rigid Rotor

(a) Consider the moment of inertia for a rigid rotor composed of two masses m_1 and m_2, which lie at distances r_1 and r_2 from the center of mass, respectively:



Show that the moment of inertia $I = m_1 r_1^2 + m_2 r_2^2$ can be written equivalently as $I = \mu r^2$ where $r = r_1 + r_2$ and μ is the reduced mass. ***Hint:*** Recall that by definition of the center of mass, $m_1 r_1 = m_2 r_2$.

(b) Consider the three rigid rotor eigenfunctions with $J = 1$:

$$Y_1^0(\theta, \phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_1^1(\theta, \phi) = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \cdot e^{i\phi}$$

$$Y_1^{-1}(\theta, \phi) = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\phi}$$

Show that each of these three functions is a solution to the rigid rotor Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

and find the corresponding energy eigenvalue.

6 A Particle on a Ring

The π-orbitals of an aromatic system like benzene, C_6H_6, may be crudely modeled using the wavefunctions and energies of a "particle on a ring." Here, we will treat the particle on a ring problem, then extend it to describe the electronic structure of benzene.

Suppose that a particle of mass m is constrained to move on a circle of radius r in the x, y plane. Assume that the particle's potential energy is a constant independent of its position with $V(x, y) = 0$.

(a) Write down the time-independent Schödinger equation in Cartesian coordinates (x, y) for this system.

(b) We will now transform our system from Cartesian coordinates (x, y) into *cylindrical* coordinates (r, θ), with

$$x = r \cdot \cos\theta$$
$$y = r \cdot \sin\theta$$

Write down the time-independent Schödinger equation in cylindrical coordinates for this system. You will want to use the fact that:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}$$

Additionally, recall that we can treat r as a constant, since the particle is constrained to move at a fixed radius.

(c) Find the general form of the solutions to this Schrödinger equation, $\psi(\theta)$.

(d) The boundary condition for this system is that the wavefunction must "wrap around," so we have $\psi(\theta) = \psi(\theta + 2\pi)$ for all values of θ.

Apply this boundary condition to your general $\psi(\theta)$ solution from part (c) and solve for the discrete energy eigenvalues that result.

Hint: You should find that $E_n = \frac{n^2\hbar^2}{2mr^2}$, $n = 0, \pm1, \pm2, \ldots$

(e) Draw an energy diagram representing the first three energy levels of this system. Make sure to note the degeneracy of each level correctly.

(f) Consider the six π electrons of a benzene molecule as particles moving on a ring of radius r. Populate your energy diagram from part (e) with these electrons, making sure to obey the Pauli principle (two electrons of opposite spin per orbital). Write down an expression for the energy it would take to excite an electron from the highest occupied molecular orbital (HOMO) to the lowest occupied molecular orbital (LUMO).